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K.U.Leuven Research and Development - Groot Begijnhof 59 - 3000 Leuven

Represented by Dr. Patrick Chaltin, T.T.O.

Patents ADP number (if you know it)

07665649003

If the applicant is a corporate body, give the country/state of its incorporation

Belgium

0318775.4

4. Title of the invention

Gluten biopolymers

5. Name of your agent (if you have one)

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GLUTEN BIOPOLYMERS

FIELD OF THE INVENTION

5 This invention relates to a modified gluten biopolymer for use in industrial applications, such as composites, stabilised foams and molded articles of manufactures. The present invention relates to a new gluten based biopolymer with modified properties, like an increased impact strength, and prepared by using thiol-
10 comprising gluten-coated fiber, its use and the method for preparing the composite material.

BACKGROUND OF THE INVENTION

15 An increase in environmental awareness has given the materials community impetus to develop cost-effective biomaterials with adequate mechanical properties. While research in recent years has led to an improved understanding of the properties of natural fibers, the problem of identifying a cost-effective biopolymer matrix material or composite material with suitable properties remains unresolved.

20

Plant proteins, such as for example wheat proteins, are interesting renewable raw materials and already a wide variety of biopolymers based on plant proteins has been used and investigated, alone or in mixtures, in order to obtain for example edible films and coatings. The plant proteins investigated include soy proteins, corn zein, wheat
25 proteins, cotton seed proteins and pea proteins and can be considered as heteropolymers.

Wheat gluten is a mixture of monomeric proteins (gliadins) and "polymerized" proteins (glutenins) linked through intermolecular disulfide bridges. The glutenins are
30 largely implicated in the viscoelastic character of gluten and gluten proteins are responsible for giving dough its strength and visco-elastic properties. Gluten can easily be isolated by removing starch and albumins/globulins by gently working a

dough under a small stream of water. After washing, a rubbery ball is left, which is called gluten. Commercially available gluten from *Amylum* contains approximately 75% protein, 10% carbohydrate, < 10% moisture, 5% lipids and < 1% minerals. The gluten proteins are furthermore very rich in glutamine and proline.

5

Although there is relatively little in the literature on the use of gluten in industrial applications, wheat gluten films have been studied in significant detail [Gennadios, A., and Weller, C. L. *Food Technol.* 1990, 44, 63-69.-3; Gontard, N., et al *J. Food Sci.* 1992, 57, 190-195.; Herald, T. J., et al *J. Food Sci.* 1995, 60, 1147-1150; Roy, S. et al *J. Food Sci.* 1999, 64, 57-60; Larré, C., et al *J. Agric. Food Chem.* 2000, 48, 5444-5449]. It has the ability to form a cohesive blend with viscoelastic properties.

Many attempts have been made to convert wheat gluten or zein into a usable biodegradable polymer (Guilbert, S. et al. *Food Add. Contam.* 1997, 14, 741; Pommet, M. et al. *Polymer* 2003, 44, 115; redl, A. et al. *Rheol. Acta* 1999, 38, 311; Pouplin, M. et al. *Agric. Food Chem.* 1999, 47(2), 538-543; di Giola, L. et al. *Agric. Food Chem.* 1999, 47, 1254). Films have been cast from gluten protein dispersions in water under different pH conditions or in ethanol [Ali, Y., et al. *Ind. Crops Prod.* 1997, 6, 177-184]. It was demonstrated that plasticizing agents could be used to improve film flexibility and decrease brittleness (Ali, Y et al. *Ind. Crops Prod.* 1997, 6, 177-184). Indeed, researchers have observed that the preparation of wheat gluten films necessitates the use of a plasticizer. In the absence of a plasticizer, gluten films are brittle and difficult to handle. A number of plasticizers have been explored in the past, including amines (diethanolamine and triethanolamine) and polyols (anhydrous glycerol, polyethyleneglycols, and polypropyleneglycols). Typical concentrations range from 10g to 60 g/100 g of dry matter [Gennadios, A., and Weller, C. L. *Food Technol.* 1990, 44, 63-69.-3, Roy, S. et al. *J. Food Sci.* 1999, 64, 57-60]. From three known plasticizers (water, glycerol and sorbitol), water was found to be the most effective plasticizer (Pouplin, M., et al. *J. Agric. Food Chem.* 1999, 47, 538).

Thus, many research has already been undertaken in order to obtain a gluten or zein based usable biodegradable polymer. However, all of these approaches encounter problems and a usable biodegradable polymer has not been described yet. For

example, previously reported experiments, designed to improve the impact strength of the gluten material require the addition of at least 10-20% (w/w) of some plasticizer, such as glycerol or triethanolamine. Furthermore, it can be argued that the formation of covalent bonds is a necessary first step in the development of a stable biopolymer system. Most of the studies presented thus far have relied on plasticizers that, at best, form only hydrogen bonds with the gluten protein chains (see references above). The use of chemical crosslinkers to modify the properties of protein-based materials have been reported as well, but to induce crosslinking with the protein structure required either the use of a catalyst (Ghorpade, V.M. et al. Trans ASAE 1995, 38, 1805; Larré, C. Agric. Food. Chem. 2000, 48, 5444) or an aggressive radiation treatment (Brault, D. Agric. Food. Chem. 1997, 45, 2964). In a more recent study of Pommert et al. the use of fatty acids was explored as a plasticizing agent for gluten. Their thermo-mechanical data revealed a "compatibility limit" between the lipid and gluten, beyond which phase separation was observed [5]. Despite the apparent incompatibility between the fatty acid and gluten, the authors maintained that a polymerization reaction had occurred between the gluten molecules and fatty acid chains.

As a summary, there is still a great need for cost-effective biomaterials with adequate mechanical properties. Therefore, a goal of the present invention is to satisfy this need by identifying a new biopolymer with interesting properties such as an increased strength, by identifying a method for increasing the impact strength of natural proteins and fibers and by producing new biodegradable composite materials. Therefore, this invention describes a method to improve the impact properties of gluten biopolymer, enabling broader usage of gluten in industrial applications. This invention also describes a new composite material and a process to make fully biodegradable composite material.

SUMMARY OF THE INVENTION

The present invention relates to a new gluten polymer matrix, with modulated material properties. The present invention also relates to the use of said gluten

polymer matrix for industrial purposes. The present invention furthermore relates to a process or a method for preparing said new polymer matrix.

The present invention also relates to a new biodegradable composite material comprising gluten and a fiber. The present invention furthermore relates to the use of
5 said composite material for industrial applications and to a process or method for preparing said composite material.

The present invention thus relates to a new gluten polymer matrix prepared by using reducing agents, more in particular thiol-containing molecules. The present invention
10 relates to a new gluten polymer matrix prepared by using thiol-containing molecules or comprising thiol-containing molecules and having modified material properties. The invention relates to a new gluten polymer matrix comprising thiol-containing molecules and with increased strain and strength, but with unaffected stiffness. The new gluten polymer matrix comprises gliadins and glutenins and proteins cross-linked
15 through thiol-containing molecules.

The present invention relates to a process for preparing the new gluten polymer matrix. The process comprises dispersing or mixing gluten in the presence of thiol-containing molecules. In a certain embodiment, the process comprises the dispersion of gluten in the presence of at least 0.1 % (w/w) versus gluten or maximally 15 %
20 (w/w) versus gluten of a thiol-containing molecule. In a particular embodiment of the invention, the thiol-containing molecule is used in stoichiometrical amounts relative to the cysteines in gluten. In a certain embodiment of the invention, the gluten can be dispersed under alkaline or acidic conditions, in aqueous environments such as alcohol-water mixtures, by using aiding agents such as hydrogen bond breakers,
25 chaotropic agents and detergents and by using other solvents such as ketones or amide solvents. In a particular embodiment the gluten is dispersed in mild acidic conditions, more particularly in an acetic acid solution, yet more in particular in 0.05 M acetic acid. In another particular embodiment the gluten is dispersed in a alcohol-water mixture, more in particular in a 50% (v/v) propanol-water solution. In another
30 embodiment of the present invention the thiol-containing molecules are selected from cysteine, dithiotreitol, mercaptoethanol, 'TP200 3MP3', 'TP70 3MP3' or 'TMP 3MP3'. Yet another particular embodiment relates to the use of polythiol-containing

molecules, more in particular hyperbranched polythiol-containing molecules. In a particular embodiment of the invention, the thiol-containing molecule used is 'TP200 3MP3'.

5 In another embodiment of the invention, the process for the preparation of the new gluten polymer also comprises an isolation step. In a certain embodiment the isolation step consists of precipitating the proteins, for example by changing the pH of the dispersion or by changing the concentration of one of the solvents used. In a particular embodiment of the invention, the precipitation is obtained by increasing the pH from mild acid conditions to a neutral pH (6.5 - 7.5), more in particular by using dilute
10 NaOH. In another embodiment the isolation step comprises the precipitation of the proteins and subsequent centrifugation.

Yet another embodiment of the process comprises the drying of the dispersion, by for example drying on the air, spray-drying or freeze-drying with or without a precipitation step or centrifugation.

15 In yet another particular embodiment, the process for the preparation of the new gluten matrix also comprises a compression-molding step. The compression molding-step consists of compression-molding the protein for several minutes, ranging from 1 to 20 minutes, more in particular from 5 to 15 minutes and yet more in particular for 10 minutes. In a certain embodiment of the process the compression-molding is
20 performed at a minimum temperature of 100°C and a minimum pressure of 150 bars for minimum 1 minute. In another embodiment the compression-molding step is performed at 150°C/200 bars for 10 minutes. In another particular embodiment the process comprises a subsequent cooling, more in particular to maximum 40°C over a period of at least 15 minutes and yet more in particular to 20°C over a period of 5
25 minutes.

The present invention furthermore relates to a process for preparing a new gluten biopolymer with modulated mechanical properties, more in particular with modulated strength, strain or stiffness, and yet more in particular with an increased strength and strain.

30 The present invention also relates to a process for improving the impact properties of gluten biopolymer with the inclusion of low levels of a thiol-containing molecule to the biopolymer/acid (preferably acetic acid) dispersion, and as modifying agent

preferably inclusion of only 1% (w/w) versus gluten or less than 1% (w/w) versus gluten of a polythiol-containing molecule, in particular a tri-thiol-containing hyperbranched molecule. A particular polythiol-containing hyperbranched molecule is tri-thiol-containing polyol mercaptoester, such as "TP200 3MP3" (Perstorp Specialty
5 Chemicals AB) (Fig. 1) or an active structural analogue thereof and the preferred acid is acetic acid. The polythiol-containing hyperbranched molecule above 0.5% (v/v), about 0.5% (v/v), from 0.5% to 0.1 % (v/v) or less than 0.1% (v/v) added to and acetic solution blended with gluten, ideally 10 ml/g.

In a further embodiment of present invention a precipitate of gluten modified by the
10 thiol-containing hyperbranched molecule, in particular by a tri-thiol-containing polyol mercaptoester and more in particular by the TP200 3MP3, can be formed by increasing the pH of the slurry from 4-4.5 to 6-6.5.

Alternatively a method can be used as described above but wherein an alcohol-based aqueous solution is used, particularly a 50% (v/v) propanol solution in place of the
15 acetic acid solution. Furthermore, the moist modified-gluten chunks (modified by the thiol-containing hyperbranched molecule, preferably by the thiol-containing polyol mercaptoester and more preferably by the TP200 3MP3) can be placed in a mold and processed at a variety of different pressures and temperatures (Fig. 2). The pressure can be gradually increased as the water in the gluten network evaporates. The gluten
20 biopolymer can also be used to extrude parts of various geometries (Fig. 3).

The present invention furthermore relates to a method for preparing a new gluten based polymer comprising the steps of dispersing and mixing the gluten in a thiol-containing molecule containing medium, precipitating the reaction products out of the medium, centrifugating the mixture, drying the precipitate and compression-molding
25 the precipitate or a combination hereof. The present invention also relates to a method for preparing a new gluten based polymer comprising the steps of dispersing and mixing the gluten in a thiol-containing molecule containing medium, drying the mixture and compression-molding the dried mixture or a combination hereof.

30 The present invention also relates to a new composite material containing fiber, characterised in that the fiber is coated with gluten. The new composite material therefore comprises fiber on which gluten is adhered. In a particular embodiment of

the invention, the fibers used in the composite material are selected from synthetic fibers, wooden fibers, nonwood fibers, natural fibers, biodegradable fibers or other fibers comprising cellulose, lignin and/or pentosans. In a more particular embodiment, the fiber is flax fiber or glass fiber.

- 5 The present invention also relates to a process for preparing said new composite materials. The present invention furthermore relates to a process for preparing the gluten-coated fiber, comprising the steps of pre-coating the fiber with gluten, placing the pre-coated fiber in an aqueous medium and drying the resulting material.

10 In a particular embodiment of the process for preparing the gluten coated fiber, the pre-coating of the fiber can be performed by sprinkling the gluten powder onto the fiber or by using the "fluidised bed" technology. In another embodiment of the process for preparing the gluten coated fiber, the pre-coated fiber is placed in a water bath for several seconds to minutes, more in particular in an alkaline or acidic water bath.

- 15 Alternatively, the present invention relates to a process for preparing gluten-coated fiber, comprising mixing a fiber in a dispersion of gluten, precipitating the gluten onto the fiber and drying the resulting material. In a particular embodiment of this process, the fibers are mixed in a dispersion of gluten, with or without thiol-containing molecules. In a certain embodiment of the invention, the gluten can be dispersed
20 under alkaline or acidic conditions, in aqueous environments such as alcohol-water mixtures, by using aiding agents such as hydrogen bond breakers, chaotropic agents and detergents and by using other solvents such as ketones or amide solvents. In a particular embodiment the gluten is dispersed in mild acidic conditions, more particularly in an acetic acid solution, yet more in particular in 0.05 M acetic acid. In
25 another particular embodiment the gluten is dispersed in a alcohol-water mixture, more in particular in a 50% (v/v) propanol-water solution. Following, the gluten can be precipitated onto the fibers or the mixture can be evaporated. In a particular embodiment of the process, the gluten is precipitated by changing the pH to approximately neutral or by changing the concentration of the solvents. Yet another
30 embodiment of the process comprises the drying of the dispersion, by for example drying on the air, spray-drying or freeze-drying with or without a precipitation step or centrifugation.

In another particular embodiment, the above mentioned steps can be followed by a compression-molding step as described above.

5 A further embodiment of present invention is a process to form a cohesive gluten polymer network around fibers. Fibers are covered by gluten powder (in certain embodiments 1/1 w/w) and consequently contacted for a short period (for instance 30 second) with alkaline water (for instance a pH 11), preferably deionised water with base, preferably NaOH or by contacted said the fibers covered by gluten powder with alkaline water, preferably deionised water with a pH of at least 8 or higher for 10 instance by dipping said mixture of said fibers and said gluten powder for less than one minute in said water. Figure 4 demonstrates gluten coating fibers, by immersing fibers with gluten powder in an alkaline water bath for less than a minute (Fig. 4). The fibers can be synthetic fibers (e.g. polypropylene fibers or polyethylene fibers) wooden fibers or nonwood fibers (e.g. flax fibers), a combination of wood and 15 nonwood fibers, natural fibers, biodegradable fibers or other fibers comprising cellulose, lignin and/or pentosans. The wood fibers or nonwood fibers can be unmodified natural fibers or can be chemically modified. The gluten biopolymer stays on the fibers even after the gluten precipitate is dried (Fig. 5).

20 An alternative approach of gluten coating of fibers is to immerse natural wood or non wood fibers in a dilute acid or dilute alcohol gluten solution. The soluble gluten molecules are allowed to interpenetrate the swelling fibers. Optionally polythiol-containing hyperbranched molecule above 0.5% (v/v), about 0.5% (v/v), from 0.5% to 0.1 % (v/v) or less than 0.1% (v/v) can be added. By increasing the pH or solvent 25 evaporation a strong adhesive bound is formed between the natural fibers and the gluten.

The gluten-coated fibers can be used to reinforce gluten composites by incorporating said gluten coated fibers into heat compression-molded gluten. The gluten-coated 30 fibers can for instance be added to the acid (preferably acetic acid) solution with thiol-containing molecules. The thiol-containing molecules can be present in amounts between 0.1% and 20 %, above 0.5% (v/v), about 0.5% (v/v), from 0.5% to 0.1 %

(v/v) or less than 0.1% (v/v) and a suspension of gluten, ideally about 10 ml/g to modify said gluten and form a precipitate by increasing the pH, ideally from 4-4.5 to 6-6.5. This fiber/gluten matrix can be compression-molded, for instance for for 10 minutes at 150 °C at a pressure of 200 bars and cooled to form a fiber reinforced
5 gluten polymer article.

The present invention furthermore relates to the industrial use of the above described materials. The materials can for example be used in the automotive, food or medical industry as materials for the construction of cars, as packaging material or as material
10 for the construction of medical devices respectively.

BRIEF DESCRIPTION OF THE FIGURES

Fig.1. Schematic of the polyol mercaptoester, TP200 3MP3, $m+n+o = 20$.

5 **Fig. 2.** Photograph of an unmodified gluten specimen (left) and TP2003MP3-modified- gluten specimen (right) obtained by the methods described. These materials were compression-molded for 10 minutes at 150 °C at a pressure of 200 bars. The temperature of the press was subsequently decreased to 20 °C before the mold was removed from the press and the parts demolded.

10

Fig. 3. Extruded parts of various geometries made from gluten biopolymer.

Fig. 4. A photograph of flax fibers covered with gluten powder, for illustrative purposes only. In the actual experiment, the flax fibers were coated manually by rolling them in the gluten powder. Afterwards, a strainer was used to support the
15 gluten powder-coated fibers as they were immersed in a 45°C alkaline (pH = 11) water bath for 30 seconds.

Fig. 5. A photograph of the gluten biopolymer/flax fiber bundle composite formed after the gluten polymer formed a precipitate around the flax fibers. After two days,
20 the gluten matrix was rigid, as most of the moisture inside the gluten polymer network had evaporated.

Fig. 6. Particle size distributions.

- 25 a. The as-received gluten powder has an average particle diameter of 50 microns.
b. The unmodified 0.01 M acetic acid-extracted gluten fraction has an average particle diameter of 20 microns.

Fig. 7. Comparison of mechanical properties of native gluten (sample 20) and thiol-
30 modified gluten (sample 22).

Fig. 8. Water absorption measurements with plain gluten and preparation 22 (as described in example 6). The data indicate a difference in molecular structure between the plain gluten and the thiol-treated gluten.

5 Fig. 9. SE-HPLC for different samples in order to evaluate the influence of molding.

a. SE-HPLC for several samples (thiol-modified or not and molded or not)

b. SE-HPLC for similar samples but after treatment with dithiotreitol (DTT) as a reducing agent.

10 The figure indicates that molded samples contain less gliadin proteins than unmolded samples. This suggests a polymerisation of gliadins in glutenins through molding (pressure and temperature raise). The data also show that by using a thiol-containing molecule more gliadins are present and thus suggests that the thiol-containing molecule acts as a reducing agent and breaks disulfide bridges.

15 Fig. 10. Mechanical properties of molded gluten specimens: Strain-to-failure

a. Samples 20, 20b and 25 are native gluten, while samples 22 and 4 were made by using stoichiometric amounts of thiol in respect of the cysteines in gluten. Specimens were molded in april.

20 b. Samples 25b, 25c, 30 and 30b are native gluten, while sample 22b was made using stoichiometric amounts of thiol in respect of the cysteines in gluten. Specimens were molded in July.

25b, 25c, etc. in the figure indicate a second or third molding from the same preparations.

h, d and w indicate measurement after one hour, one day or one week respectively and show that there is a high standarddeviation in the results and a high dependence of time, although a significant differences between the samples is present.

Fig. 11. Mechanical properties of molded gluten specimens: Strength

For the same samples and under the same conditions as in figure 10.

30

Fig. 12. Mechanical properties of molded gluten specimens: Stiffness

For the same samples and under the same conditions as in figure 10.

Fig. 13. Picture of mold without and with a gluten sample.

Fig. 14. Strain, strength and stiffness of several samples: regular commercially available gluten (Reg.Glu), samples 18, 20, 21, 22, 23 and 24 (as explained in example 6). The cubes from left to right reflect measurements 1 hour, 1 day and 1 week after molding respectively.

10 DETAILED DESCRIPTION OF THE INVENTION

The terminology used herein is for the purpose of describing particular embodiments only, and is not intended to limit the scope of the present invention.

15 Definitions

As used in the specification and the appended claims, the terms "fibers" and "fibrous materials" include both inorganic fibers or fabric and organic fibers and fabric. In general, fibers can be classified into three categories: wood, nonwood, and nonplant.

20 Fibers that may be incorporated into gluten matrix preferably include naturally occurring organic fibers, such as cellulosic fibers extracted from hemp, cotton, plant leaves, sisal, abaca, bagasse, wood (both hardwood or softwood, examples of which include southern hardwood and southern pine, respectively), or stems, husks, shells, and fruits or any nonwood fiber as defined hereunder, or inorganic fibers made from
25 glass, graphite, silica, ceramic, or metal materials. Any equivalent fiber which imparts strength and flexibility is also within the scope of the present invention.

The term "nonwood fibers" as used herein is thus to distinguish plant fibers from wood fibers (softwood or hardwood), the fibers can be derived from selected tissues of various mono- or dicotyledonous plants. And are categorized botanically as grass,
30 bast, leaf, or fruit fibers. The nonwood fibers can also be classified by means of production such as sugar cane bagasse, wheat, straw and corn stalks byproducts. They can also be grouped as "fiber plants", plants with high cellulose content that are

cultivated primarily for the sake of their fibers such as jute, kenaf, flax, cotton and ramie. An example of nonwood fibers are fibers consisting of the group of Jute, flax, cotton, Hemp, Kenaf, Pina, Abaca, Sisal, Hennequen, Stalk (Rice, Wheat, Barley, Oat, Rye), Cane (Sugar, Bamboo), Grass (Esparto, Sobai), Reed (e.g. Phragmites communis), Bast (Seed flax, Kenaf, Jute, Hemp, Ramie), core (Kenaf, Jute), Leaf (Abaca (e.g. Manila), Sisal (e.g. Agave)), Seed hull (e.g. cotton linter).

The term "thiol-containing molecule(s)" as used herein refers to molecules with at least one free thiol group, particularly a thiol group that has a free electronpair and in a particular case have reducing capacity. The molecules can be straight, branched or hyperbranched. Examples of polythiol-containing molecules are cysteine, dithiotreitol, mercaptoethanol, 'TP200 3MP3', 'TP70 3MP3' or 'TMP 3MP3' (Perstorp Speciality Chemicals), the three last ones differing with respect to their degree of ethoxylation (the first carries twenty ethylene oxide units, the second carries seven, and the last does not carry any ethylene oxide units at all). 'TP200 3MP3' has a high flexibility and water compatibility.

The term "gluten" as used herein refers to the commercially available wheat gluten from for example Amylum (Aalst, Belgium). The term gluten however also refers to gluten as a composition containing gliadins and glutenins. It is however clear to a person skilled in the art that gluten as used in this invention can also mean any composition containing at least 50% storage proteins derived from a plant, or more particularly from a cereal, yet more particularly from a prolamine rich cereal and yet more in particular from wheat, barley, rye, maize or soy. The term can also refer to fractions of all the above described compositions.

It is also clear to a person skilled in the art that "gluten" could also refer to a synthetic mixture which is analogous to the gluten obtained from naturally occurring plants.

The present invention shows that gluten can be formed into a tough plastic like substance by using thiol-containing molecules during its preparation. This led to the possibility of developing biodegradable high performance engineering plastics and

composites from renewable resources that are far less expensive than their synthetic counterparts. The present invention showed that an otherwise brittle protein-based material could be toughened by doubling the yield stress and strain to failure, without compromising stiffness.

5

In the present work, the fracture toughness of the gluten polymer was improved by a factor of ten or more with the addition of a thiol-containing molecule such as a tri-thiol-containing modifying agent (with less than 1% (w/w) used). The thiol-containing molecules have another notable attribute, namely, that under proper chemical and environmental conditions, it has the potential to bond chemically with the gluten biopolymer via sulphhydryl/disulfide exchange reactions, giving rise to a potentially more stable material (e.g. a stabilised gluten foam). In addition, the process does not require the addition of other solubilizing agents, such as reducing agents or salts, to obtain a homogeneous dispersion. When glutenin chains are synthesized, two cysteine residues on each chain preferentially form interchain disulphide bonds (SS) resulting in linear arrays of polypeptide chains.

10

The present invention relates to the incorporation of thiol-containing molecules, for instance TP200 3MP3 from Perstorp Specialty Chemicals AB, into the gluten biopolymer with the possibility of crosslinking it with the gluten network, giving rise to a tougher material system. Inherent challenges in processing gluten are attributed to the low solubility of gluten in most solvents, as well as its high melt viscosity.

15

Results of the research showed that when a thiol-containing molecule was used in the preparation of the gluten polymer and possibly incorporated into the network structure of the gluten polymer, material's strain-to-failure and strength can be increased without compromising stiffness (Figures 10, 11 and 12). Furthermore, water absorption results indicate that the presence of a thiol-containing molecule leads to an increase in molecular crosslink density (Figure 8). Finally, HPLC data of molded thiol-modified gluten are consistent with that of a polymer that has been further crosslinked (Figure 9).

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30

Another important aspect is that the results show that there is a certain aging effect that further improves the mechanical properties of the new gluten biopolymer (Figures 10, 11 and 12)

- 5 The research also resulted in the development of gluten biopolymer-modified fiber (flax or glass) and bundle, demonstrating a process to make fully biodegradable composite materials. Qualitative analysis suggests that a strong interface between the natural fibers and biopolymer matrix can form spontaneously under the proper conditions, precluding the need to rely on more traditional chemical treatments to
10 promote fiber/matrix adhesion.

In order to be able to chemically modify gluten or to coat gluten on fibers, gluten needs to be dispersed. Several methods for the preparation of chemically modified gluten or gluten coated fibers described, use a dispersion of gluten. Several methods
15 and agents can be used to obtain a dispersion of gluten:

- *(Mild) acidic/alkaline conditions:* Probably the most gentle way to disperse gluten, is to bring the gluten in an environment with a decreased pH. Decreasing the pH (around 4 or lower, with for example HCl in water, dilute acetic acid or lactic acid) allows to solubilise a part of the gluten proteins and surely allows to make a
20 homogenous "dispersion" of the total gluten. Also alkaline conditions (f.e. NaOH in water) allow to make a homogenous dispersion.

However, strong alkaline or acid conditions will further help solubilising gluten but will affect the protein structure (deamidation, modification of some amino acids, peptide bond hydrolysis, etc.).

- 25 An advantage of dispersing under (mild) acidic or alkaline conditions is that proteins can be precipitated by a simple change in pH towards neutral where gluten proteins are totally insoluble. This type of precipitation can then be applied after putting fibers in a gluten dispersion to make the gluten proteins efficiently stick to the fiber material.

- 30 • *Aqueous alcohol solutions:* Alcohol/water mixtures are very often used in gluten research to solubilise part of the gluten proteins (ca 50 % can be solubilised) and the total gluten can be homogeneously dispersed in alcohol/water mixtures. Mixture of 70% ethanol or 50% propanol can for example be applied for this

purpose. Some other proteins, like for example corn zeins (the "gluten" equivalent from corn) are soluble in pure methanol.

The fact that gluten proteins are only soluble/dispersible at certain alcohol concentrations offers the possibility to precipitate them by changing this concentration (adding more alcohol or by dilution with water). The alcohol can also be removed by evaporation.

- *aiding agents*: Several agents are often used in gluten research either in pure water or in one of the above solvents to aid solubilisation of gluten proteins. Often several agents are combined to solubilise gluten proteins. However, protein structure is nearly always affected in this way.

Following aiding agents are used:

a/ reducing agents (e.g. sulfites, cysteine, glutathione, dithiothreitol): by lowering the molecular weight of the proteins they enhance their solubility (obviously they also drastically change their structure and functionality)

b/ hydrogen bond breakers (e.g. urea)

c/ chaotropic agents (e.g. guanidinium hydrochloride)

d/ detergents (e.g. sodium dodecyl sulfate, cetyl trimethyl ammonium bromide)

e/ salts: increasing the ionic strength is known to decrease the solubility of gluten proteins. However, in the literature it can also be found that incubation of gluten in salt would increase the solubility of gluten proteins in distilled deionised water.

- *other solvents*: Literature describes the use of other solvents (e.g. ketones, amide solvents) for these purposes (f.e. solubilisation of zeins).

Drying of materials can be performed in several ways. Materials can be dried on the air, by using spray-drying or freeze-drying. The materials can also be placed in an exicator or a heating gun, combined with water attracting compounds. The solvents in a mixture can furthermore also be evaporated by using a rotovapor, or by applying vacuum. Spray-drying can for example be performed under the following conditions: compressed air $P = 4$ bars; inlet $T = 130$ °C and outlet $T = 95 - 105$ °C.

The fluidised bed technology can also be used in the invention in order to pre-coat the fibers with gluten. With for example ETT's E-Preg[®] process, carbon fiber or fiberglass

fabric is passed through a special electrostatic fluidized bed coater capable of depositing (gluten) powder on both sides of the web. Electrostatic attraction causes the powder to adhere to the substrate, which is then passed through an oven to melt and flow the powder into or onto the fiber.

5

General methods and materials

Commercial wheat gluten [70.2% protein content on dry basis as determined by the Kjeldahl method ($n \times 5.7$)] from Amylum (Aalst, Belgium) was used in this study.

10

Preparation of a new gluten biopolymer by using thiol-containing molecules

The chemical modification of gluten can in general be obtained through mixing gluten with a thiol-containing molecule in an aqueous medium. By subsequent compression molding a material with modified properties is obtained.

15 The thiol-containing molecule was added in amounts calculated in respect to the experimentally determined cysteine content in the gluten (gluten contains approximately 13.8 mmol thiol function - this can be derived from the amount of cysteine in gluten). As an example, the principle of a 1:1 stoichiometric mixture can be applied to allow one mole of TP200 3MP3 SH groups to interact with one mole of
20 gluten cysteine groups. The basic procedure involved preparing a gluten dispersion containing the thiol-containing compound and leaving the mixture to stir overnight, mostly in a refrigerator (6-8°C). The following day the contents were dried (i.e. freeze-dried) over a certain period (i.e. four days). Afterwards, the dried contents were
25 homogenized using a mortar and pestle, passed through a micron-size sieve, and put on a rotating shaker overnight. Specific details pertaining to individual samples are provided below.

Compression molding

30 Compression molding was always performed with thiol-modified gluten and gluten coated fibers to produce a molded material. Specimens and gluten samples can be compression molded by applying a certain pressure and temperature, i.e. at 200 bars/150°C for 3 to 15 min. Specimens were prepared in a 10 cavity mold. The mold

was carefully prepared using a mold release agent, previously applied and cured before gluten powders were used.

Preparation of gluten coated fibers

- 5 The general method used in order to obtain a gluten coated fiber was to bring the fiber into contact with gluten in an aqueous environment. In one method the gluten is pre-coated with gluten powder by sprinkling or by the fluidised bed method.

Mechanical property determination

10

Tensile Test: The 10 specimens prepared from each molding exercise were used in tensile tests. Specimens were tested within 1 hour of molding, after 24 hours, and after 7 days. At each testing time, 3 of the specimens were used. In those cases where 10 high quality specimens were obtained, the 10th specimen is being saved for evaluation after several months. All specimens were stored at ambient conditions so the tests after 24 hours and after 7 days provide preliminary indications of temporal stability of the material. The tests were conducted on a computer interfaced Instron 1011 with a 1000 Lb load cell. Load data were collected at a rate of 10 s⁻¹, and each test was repeated 3 times. The stress strain curves (Figure 7) were evaluated to provide modulus, failure strain, and yield strength. Modulus was determined by fitting a straight line to the stress strain curves in the early region at strains below ½ %.

15

Charpy Impact test: For the measurement of fracture toughness, the Charpy impact test could be applied and was conducted in accordance with ISO-Norm 179.

Three point bend test: the three point bend test was performed as described in literature and is well known to a person skilled in the art.

25

Water absorption studies: the water absorption studies were performed as described in literature and is well known to a person skilled in the art.

Molecular weight determination: Size exclusion- high performance liquid chromatography (Se-HPLC)

30

Samples were dissolved (2.5 mg/2.5 ml) in a phosphate-sodium dodecyl sulphate (SDS) buffer [0.05M sodium phosphate, approximately pH 6.8, containing 2.0% (w/v) SDS], filtered (approximately 0.45 µm) and a fraction was loaded on a Phenomenex

BioSep-SEC-S4000 (300 mm x 7.8 mm) column (Phenomenex, Torrance, CA, USA). The proteins were eluted at room temperature with 50% (v/v) acetonitrile containing 0.05% (v/v) trifluoroacetic acid (flow rate: 0.5 ml/min). Reduced protein samples were obtained by adding 1 % (w/v) dithiothreitol to the phosphate-SDS buffer. The detection was performed with a Kontron HPLC 332 detector (Kontron Instruments Ltd, Buckinghamshire, UK) at 210 nm. Proteins were classified into three groups: insoluble polymeric protein, soluble polymeric protein, and monomeric protein. The proportion of insoluble protein was calculated from peak areas of reduced and unreduced samples in the chromatograms (Verbruggen, I.M. et al. J. Cereal Sci. 2003, 37, p. 151).

Examples

Example 1

Comparison of the mechanical properties of plain gluten (tensile strength, apparent modulus, and impact strength) with those of several synthetic materials, comprising polypropylene, epoxy, low-density polyethylene (PE), and high-density polyethylene PE (table 1)

Polymer	Apparent E-modulus (MPa)	Tensile Strength (MPa)	Charpy Impact Strength (kJ/m ²)
Gluten	3555	43	2.48
Polypropylene	1000-1600	31-37	14
Epoxy	2600-3800	50-79	7.5
Low density PE	100-260	10-12	39
High density PE	410-1240	26-33	68

Table 1. Mechanical properties of various polymers as they compare with gluten matrix material processed at 150 °C/72 bars as measured by the Three-Point-Bend test.

The apparent E-modulus and tensile strength of wheat gluten seems on par with a number of commonly used synthetic polymers. However, a drawback is the fact that the impact strength of cured gluten is relatively low. The impact strength increased when glycerol was added to the matrix, however this results in the lowering of the E-modulus and tensile strength.

Example 2

The thiol molecule, 'TP200 3MP3', was employed in this example. Gluten powder (150 g) was added slowly (over a period of 1 ½ hrs at room temperature) to 1.5 L 0.05 M acetic acid solution containing 0.1% (v/v) of 'TP200 3MP3'. The mixture was stirred continuously as the gluten powder was added to the solution. The dispersion was put on a shaker in a refrigerator and left overnight. A homogeneous dispersion of the gluten proteins in the acetic acid was obtained, enabling the 'TP200 3MP3' molecule to interact directly with the gluten proteins. The material was recovered by precipitation upon increasing the pH (from 4.5 to 6.5) by addition of dilute NaOH. Afterwards, the gluten/solvent mixture was separated by centrifugation (10,000 g, 20 °C, 15 min) and the modified-gluten precipitate was stored in a refrigerator until further use. The molded material could then be obtained by compression molding the previously prepared powder.

20

Example 3

In this experiment, a 50% (w/w) propanol/water solution was used in place of the acetic acid solution, and the solvent was evaporated by 'rotavapping' the modified-gluten/solvent mixture at 50 °C. However, subsequent removal of the dried biopolymer from the glass flask was difficult due to the strong adhesion between the gluten network and the glass. To be able to easily remove the biopolymer, before all the propanol is evaporated, dilute acetic acid can be added.

Upon incorporating 0.1 % (w/w) of 'TP200 3MP3' in a 50% (v/v) propanol solution, the fracture toughness of molded gluten was increased from 3 kJ/m² to an average of 36 kJ/m² as measured by the Charpy Impact test. Individual fracture toughness measurements of four six-day-old TP2003MP3-modified gluten specimens included the following: 47.1 kJ/m², 24.2 kJ/m², 34.2 kJ/m², and 39.2 kJ/m². Specimens were

30

compression-molded at 150 °C/200 bars for 10 min. and subsequently cooled to 20 °C over a period of 5 min. An unmodified control sample yielded a Charpy impact strength of 3.2 kJ/m² (Iso Norm 179 standard analysis).

5 Example 4: Preparation and investigation of gluten coated flax fibers

A bundle of flax fiber was pre-coated with gluten powder by sprinkling the gluten powder onto the fibers, which was then placed between two metal strainers. A dilute alkaline (NaOH) water bath was prepared (as acidic conditions are known to be detrimental to flax fibers). Two strainers were used to contain the coated fiber bundle, which was then dipped in the alkaline water bath for 30-60 sec. The hydrated gluten formed a precipitate almost immediately, resulting in a gluten-encapsulated fiber bundle. The gluten-coated fiber bundle was left to dry in ambient conditions for a period of several days and yielded the new composite material, namely gluten coated flax fiber. The gluten coated fibers remain intact after several months.

15 Example 5: Preparation of gluten coated glass fibers

For the purpose of preparing the gluten coated glass fibers, the standard "Fiber-Tow Impregnation Line" or "Fluidized Bed" technology was applied. In this experiment, a commercial grade-glass fiber: "2400 P 319 E1" from Owens Corning was used. The airflow of the fluidized chamber was set at 0.2 bars and the vibration at 7 bars. The oven temperatures were set at 120-170°C and 175 °C, respectively, and the rollers inside the oven were removed. The oven was not used to melt the gluten, but merely, to dry the fibers. As the gluten powder coated fiber was drawn from the fluidized bed, water was applied manually using either a water bath or a squirt bottle for bringing the gluten molecules in close proximity with the fiber surface.

25 Example 6: Chemically modified gluten polymers prepared during experiments with their referred sample numbers

- 30 1) plain gluten; solvent used 0.05M AcOH; contents freeze-dried, milled, and passed through a 250 micron sieve
- 2) gluten + 1% (w/w) TP703MP3; solvent used: 0.05 M AcOH; contents freeze-dried, milled, and passed through a 250 micron sieve

- 3) gluten + 1% (w/w) TP2003MP3; solvent used: 0.05 M AcOH; contents freeze-dried, milled, and passed through a 250 micron sieve
- 4) gluten + 5.8% (w/w) TP2003MP3; solvent used: 0.05 M AcOH; contents freeze-dried, milled, and passed through a 250 micron sieve
- 5) 5) gluten + 1% (w/w) TP2003MP3; solvent used 50% PrOH; contents freeze-dried, and homogenized with a mortar and pestle
- 6) plain gluten; solvent used 70% EtOH; contents freeze-dried (twice), homogenized with a mortar and pestle, passed through a 400 micron sieve, and put on rotating shaker overnight
- 10 7) gluten + 0.1% (w/w) DTT; solvent used: 70% EtOH; contents freeze-dried (twice), homogenized with a mortar and pestle, passed through a 400 micron sieve, and put on rotating shaker overnight
- 8) gluten + 0.1% (w/w) DTT + 0.5% (w/w) KIO₃ (present in excess); solvent used 70% EtOH; contents freeze-dried (twice), homogenized with a mortar and pestle, passed through a 400 micron sieve, and put on rotating shaker overnight
- 15 9) gluten + 0.1% (w/w) DTT + 1% (w/w) TP2003MP3 + 0.5% (w/w) KIO₃ (present in excess); solvent used: 70% EtOH; contents freeze-dried (twice), homogenized with a mortar and pestle, passed through a 400 micron sieve, and put on rotating shaker overnight
- 20 10) gluten + 0.1% (w/w) DTT + 1% (w/w) TP2003MP3; solvent used: 70% EtOH; contents freeze-dried (twice), homogenized with a mortar and pestle, passed through a 400 micron sieve, and put on rotating shaker overnight
- 11) plain gluten; solvent used 70% EtOH; contents freeze-dried (twice), homogenized with a mortar and pestle, passed through a 400 micron sieve, and put on rotating shaker overnight.
- 25 18) gluten + 6.5% (w/w) China reed fibers; solvent used 0.05M AcOH; contents freeze-dried (twice), homogeneous on a macroscopic scale; mortar and pestle *not* used to avoid fiber breakage
- 19) gluten + 29.4% (w/w) China reed fibers; solvent used 0.05M AcOH; contents freeze-dried (twice), inhomogeneous on a macroscopic scale; mortar and pestle *not* used to avoid fiber breakage
- 30

- 20) plain gluten; solvent used 0.05 M AcOH; contents freeze-dried, homogenized with a mortar and pestle, passed through a 400 micron sieve, and put on rotating shaker overnight
- 5 21) gluten + 0.55% (w/w) cysteine; solvent used 0.05 M AcOH; contents freeze-dried, homogenized with a mortar and pestle, passed through a 400 micron sieve, and put on rotating shaker overnight
- 22) gluten + 5.8% (w/w) TP2003MP3; solvent used 0.05 M AcOH; contents freeze-dried, homogenized with a mortar and pestle, passed through a 400 micron sieve, and put on rotating shaker overnight
- 10 23) gluten + 3.2% (w/w) TP703MP3; solvent used 0.05 M AcOH; contents freeze-dried, homogenized with a mortar and pestle, passed through a 400 micron sieve, and put on rotating shaker overnight
- 24) gluten + 3.2% (w/w) TP703MP3 + 0.5% KIO₃; solvent used 0.05 M AcOH; contents freeze-dried, homogenized with a mortar and pestle, passed through a 400 micron sieve, and put on rotating shaker overnight
- 15 25) plain gluten; solvent used 0.05 M AcOH; contents freeze-dried, homogenized with a mortar and pestle, passed through a 400 micron sieve, and put on rotating shaker overnight
- 26) gluten + 1.7% (w/w) cysteine; solvent used 0.05 M AcOH; contents freeze-dried, homogenized with a mortar and pestle, passed through a 400 micron sieve, and put on rotating shaker overnight
- 20 27) gluten + 1.0% (w/w) DTT; solvent used 0.05 M AcOH; contents freeze-dried, homogenized with a mortar and pestle, passed through a 400 micron sieve, and put on rotating shaker overnight
- 28) gluten + 11.6% (w/w) TP2003MP3; solvent used 0.05 M AcOH; contents freeze-dried, homogenized with a mortar and pestle, passed through a 400 micron sieve, and put on rotating shaker overnight
- 25 29) gluten + 11.2% (w/w) TP200 polyol; solvent used 0.05 M AcOH; contents freeze-dried, homogenized with a mortar and pestle, passed through a 400 micron sieve, and put on rotating shaker overnight
- 30

- 30) plain gluten; solvent used 0.05 M AcOH; contents freeze-dried, homogenized with a mortar and pestle, passed through a 400 micron sieve, and put on rotating shaker overnight
- 5 31) gluten + 5x[5.8% (w/w) TP2003MP3]; solvent used 0.05 M AcOH; contents freeze-dried, homogenized with a mortar and pestle, passed through a 400 micron sieve, and put on rotating shaker overnight
- 32) gluten + 10x[5.8% (w/w) TP2003MP3]; solvent used 0.05 M AcOH; contents freeze-dried, homogenized with a mortar and pestle, passed through a 400 micron sieve, and put on rotating shaker overnight
- 10 33) gluten + 15x[5.8% (w/w) TP2003MP3]; solvent used 0.05 M AcOH; contents freeze-dried, homogenized with a mortar and pestle, passed through a 400 micron sieve, and put on rotating shaker overnight

Example 7: results of experiments

- 15 The strain, strength and stiffness of several samples has been measured. Results are shown in figures 10, 11, 12 and 14. The results show an increase in strain and strength, while the stiffness remains unaffected for thiol-modified gluten polymers and for gluten-coated fibers.

CLAIMS

- 1) A composite material comprising fiber, characterised in that the fiber is coated with gluten.
- 5 2) A composite material as in claim 1, wherein the gluten is modified by thiol-containing molecules.
- 3) A process for preparing a composite material of claim 1, characterised in that the process comprises the steps of pre-coating the fiber with gluten, placing the pre-coated fiber in an aqueous environment and drying the resulting material.
- 10 4) A process for adhering gluten to fiber, comprising mixing gluten and fiber in an aqueous environment.
- 5) A gluten polymer matrix with modulated material properties resulting from the use of a thiol-containing molecule during the preparation of the gluten polymer.

ABSTRACT

This invention consists of a modified gluten biopolymer for use in industrial applications, such as composites and foams. In the present work, the fracture toughness of the gluten polymer was improved with the addition of a thiol-containing modifying agent. This work also resulted in the development of a gluten biopolymer-modified fiber bundle, demonstrating the potential to process fully biodegradable composite materials. Qualitative analysis suggests that a reasonably strong interface between the natural fibers and biopolymer matrix can form spontaneously under the proper conditions.

Therefore this invention relates to a modified gluten biopolymer for use in industrial applications, such as composites, stabilised foams and molded articles of manufactures. The present invention relates to a new gluten based biopolymer with modified properties, like an increased impact strength, and prepared by using thiol-containing molecules. The invention furthermore relates to a new composite material comprising gluten-coated fiber, its use and the method for preparing the composite material.

FIGURES

Fig.1.

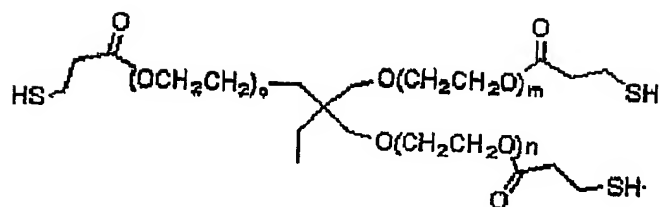


Fig. 2.

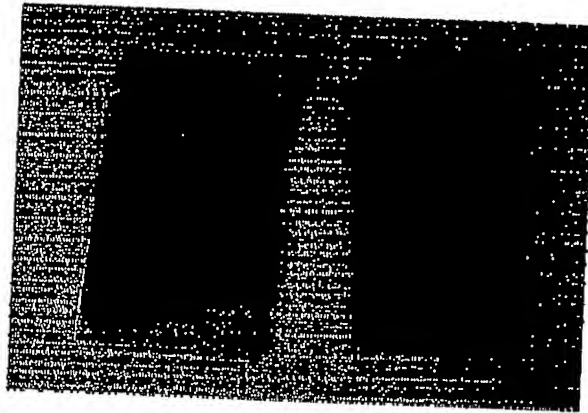


Fig. 3.



Fig. 4

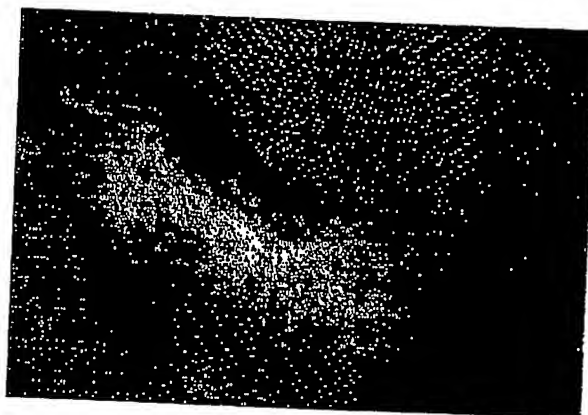
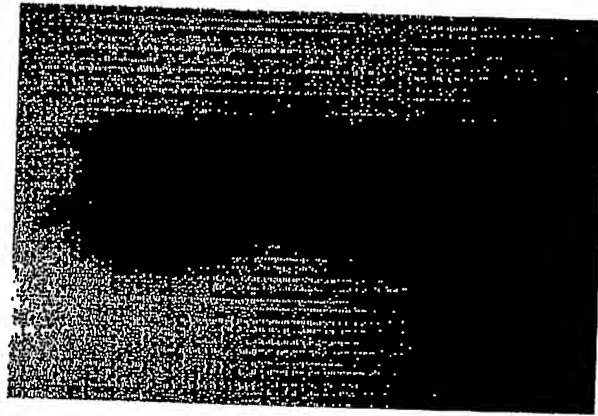


Fig. 5.



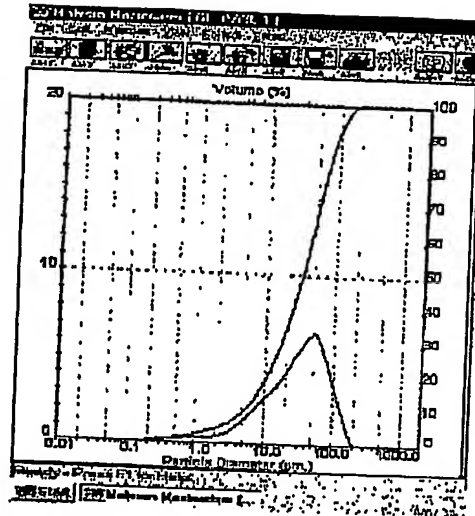


Fig. 6 a

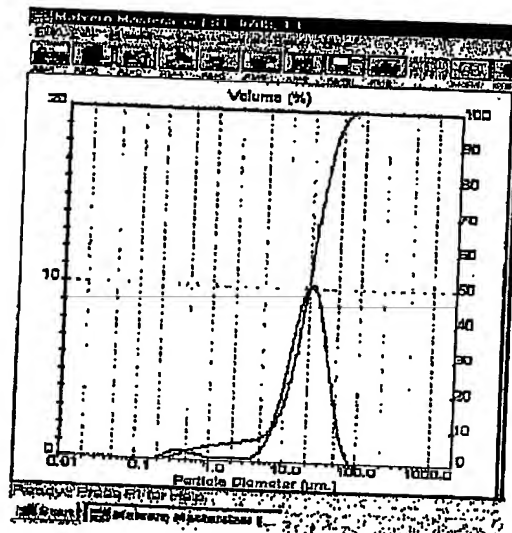


Fig. 6 b

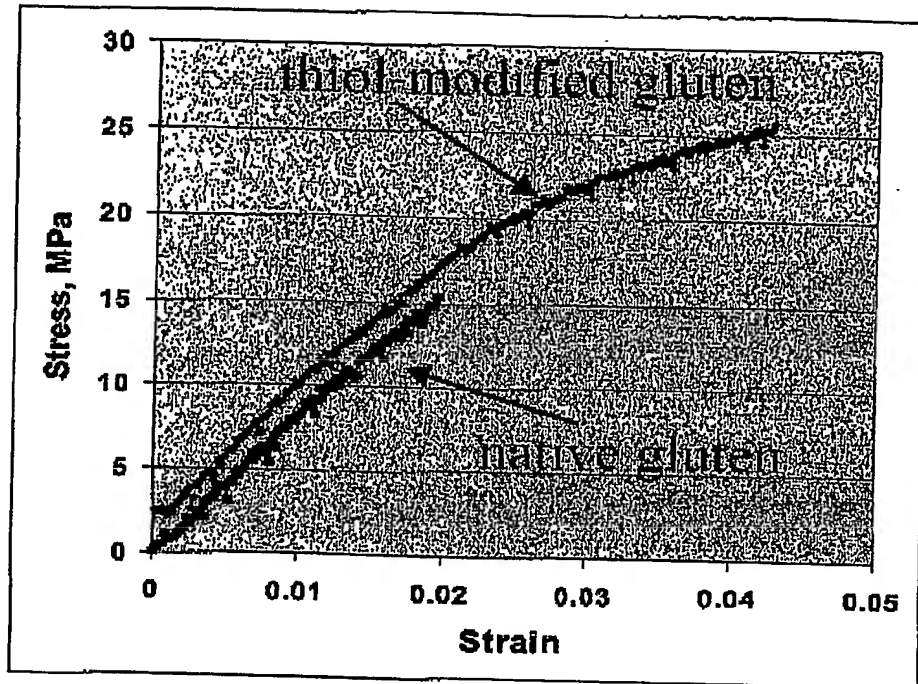


Fig 7

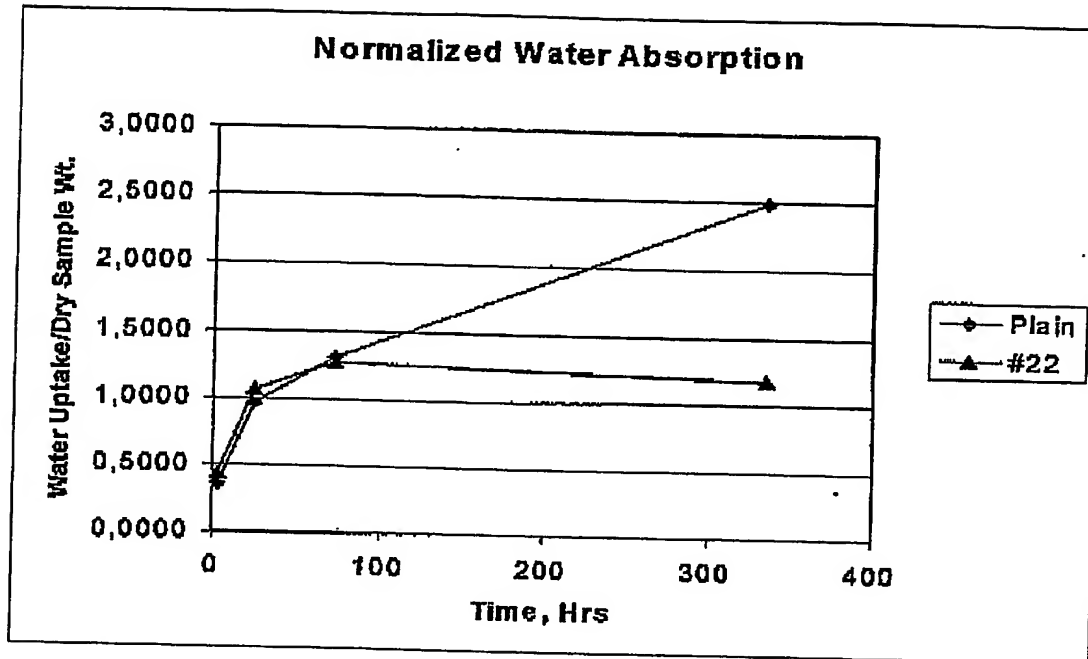
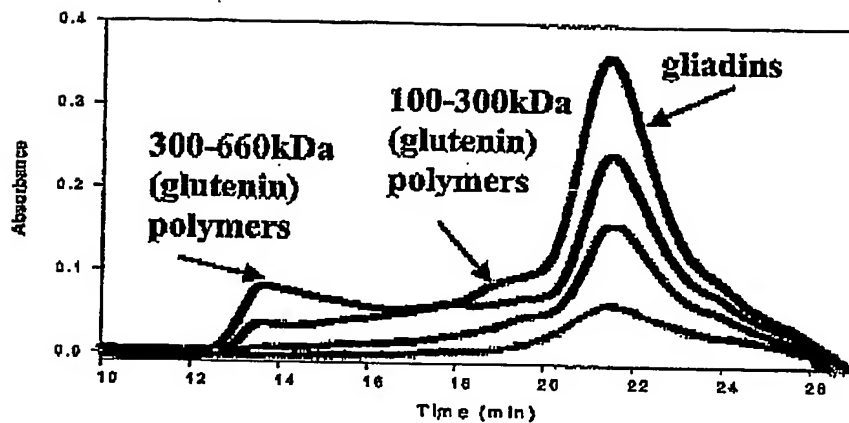


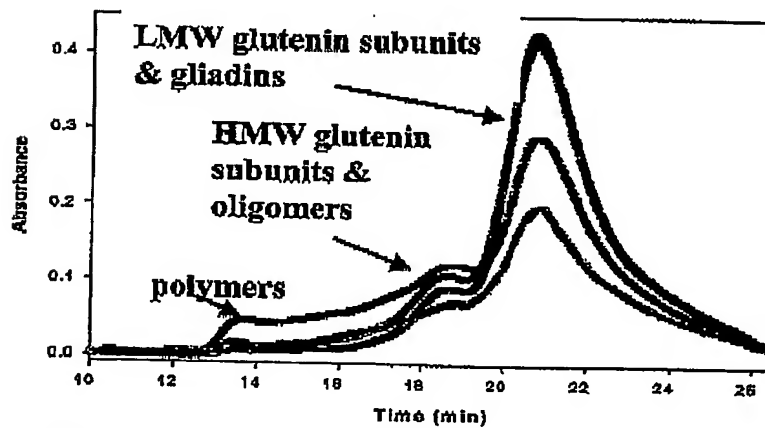
Fig. 8



From top to bottom at the peak around 21 min.:

- thiol-modified gluten before molding
- native gluten before molding
- native gluten after molding
- thiol-modified gluten after molding

Fig 9 a



From top to bottom at the peak around 21 min.:

- thiol-modified gluten before molding
- native gluten before molding (practically converged with upper curve)
- native gluten after molding
- thiol-modified gluten after molding

Fig. 9 b

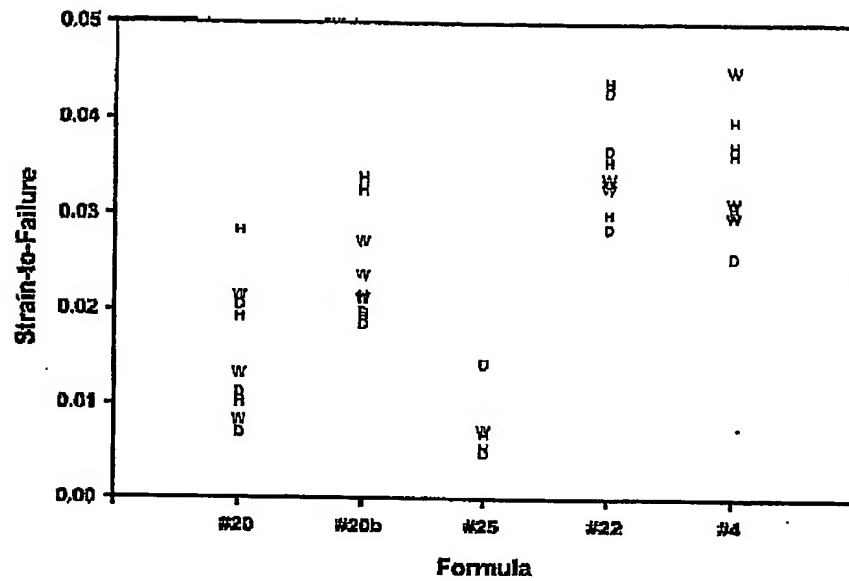


Fig. 10 a

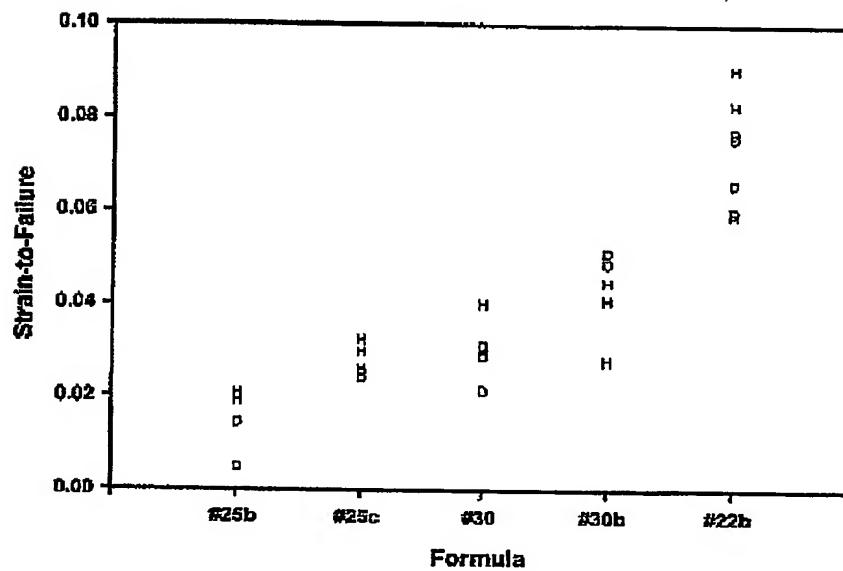


Fig. 10 b

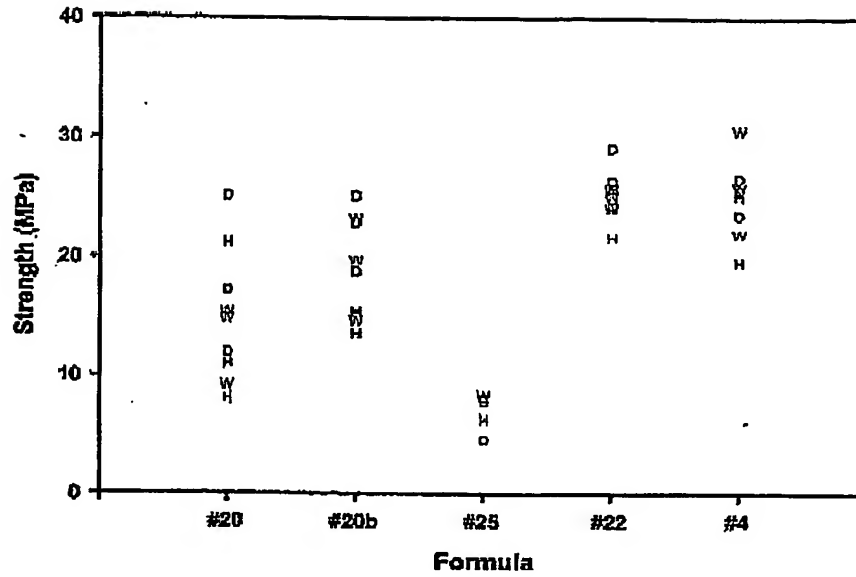


Fig. 11 a

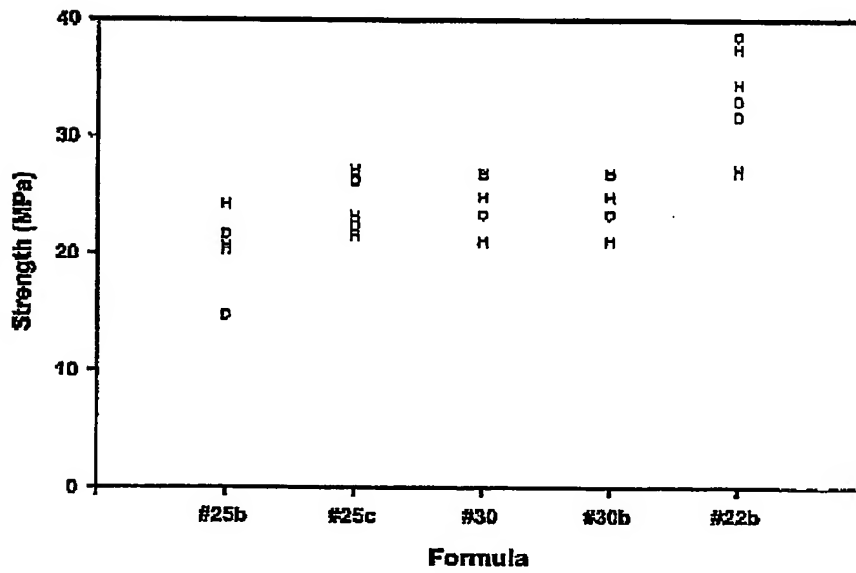


Fig. 11 b

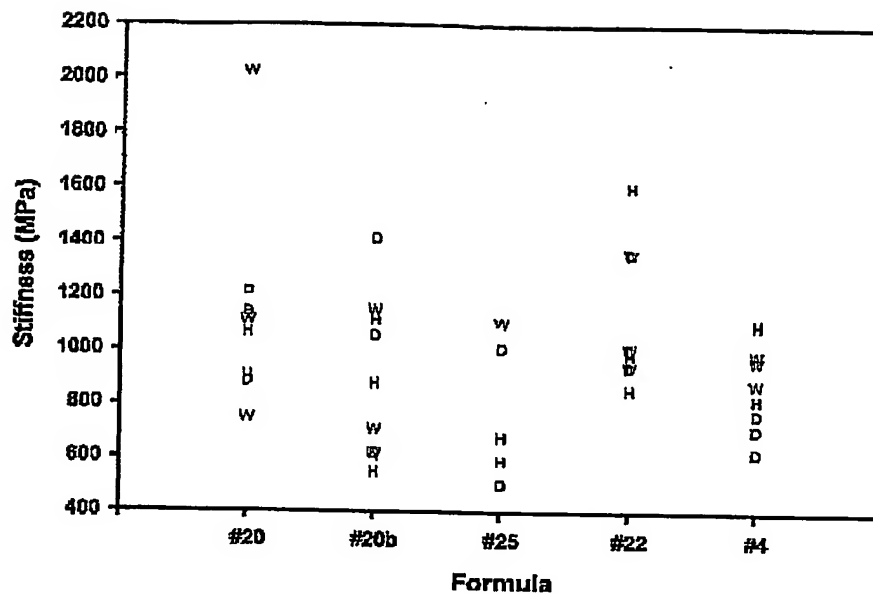


Fig. 12 a

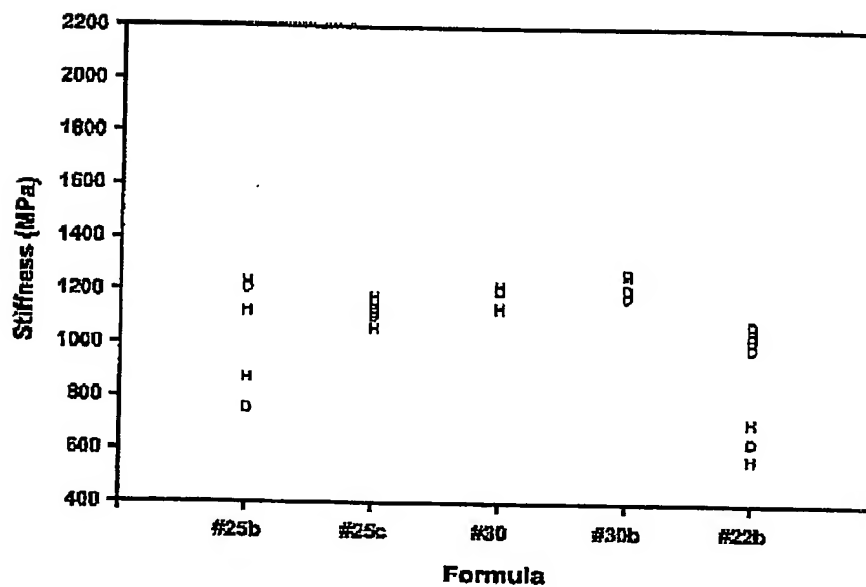
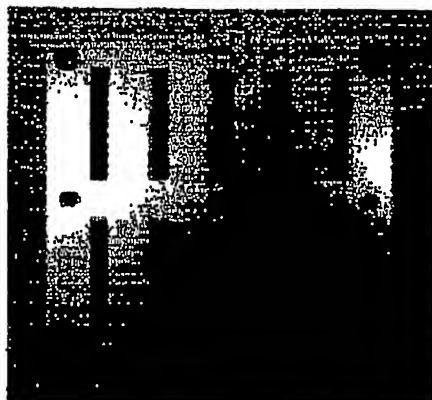
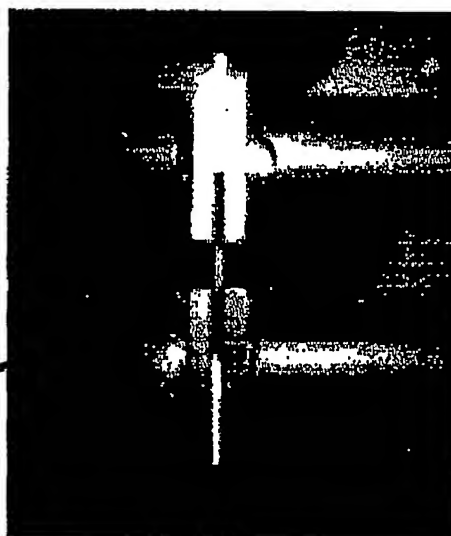


Fig. 12 b



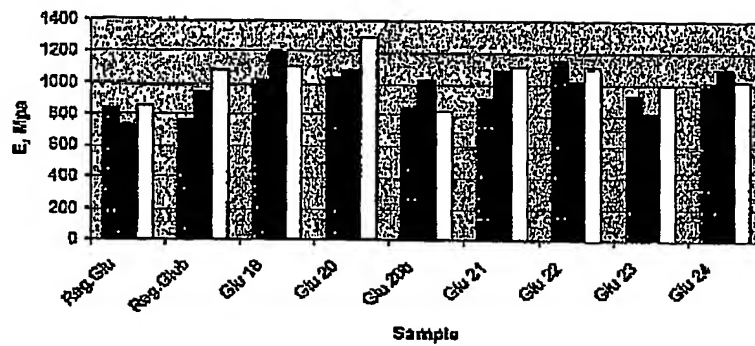
mold



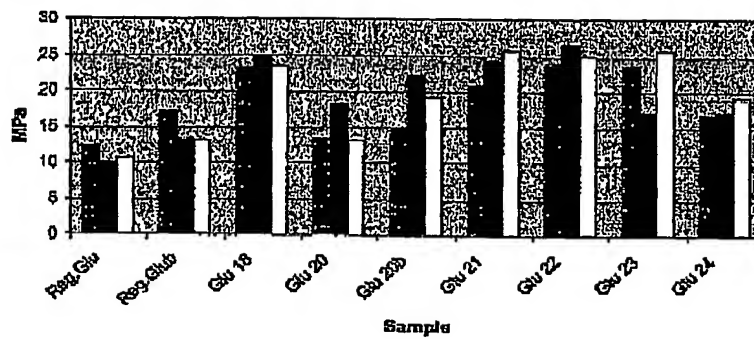
specimen

Fig. 13

a) Stiffness



b) Strength



c) Strain

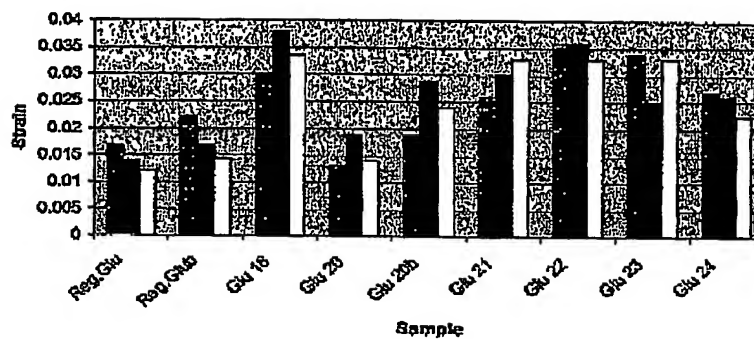


Fig. 14

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